

Thermoelectric Properties in the $\text{TiO}_2/\text{SnO}_2$ System

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Nanotechnology has provided a new interest in thermoelectric technology. A thermodynamically driven process is one approach in achieving nanostructures in bulk materials. $\text{TiO}_2/\text{SnO}_2$ system exhibits a large spinodal region with exceptional stable phase separated microstructures up to 1400 °C. Fabricated $\text{TiO}_2/\text{SnO}_2$ nanocomposites exhibit n-type behavior with Seebeck coefficients greater than -300 $\mu\text{V/K}$. Composites exhibit good thermal conductance in the range of 7 to 1 W/mK. Dopant additions have not achieved high electrical conductivity ($<1000 \text{ S/m}$). Formation of oxygen deficient composites, $\text{Ti}_x\text{Sn}_{1-x}\text{O}_{2-y}$, can change the electrical conductivity by four orders of magnitude. Achieving higher thermoelectric ZT by oxygen deficiency is being explored. Seebeck coefficient, thermal conductivity, electrical conductance and microstructure will be discussed in relation to composition and doping.



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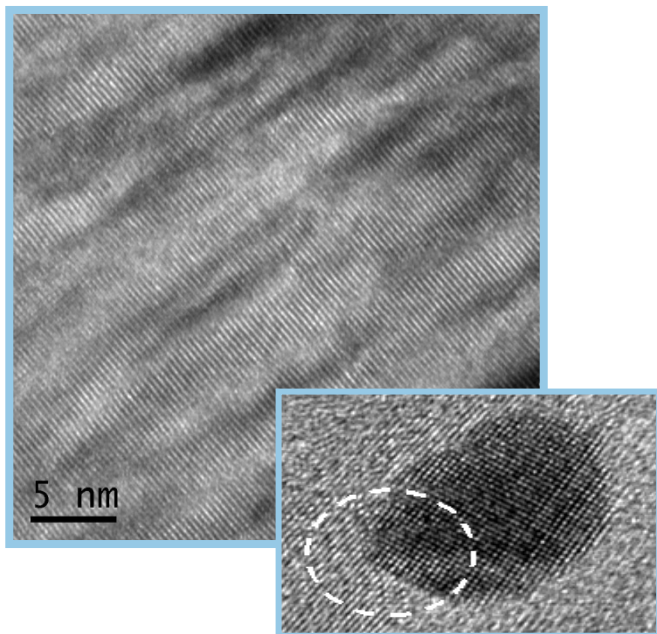
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Alp Sehirliglu,

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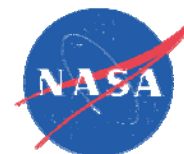
USA



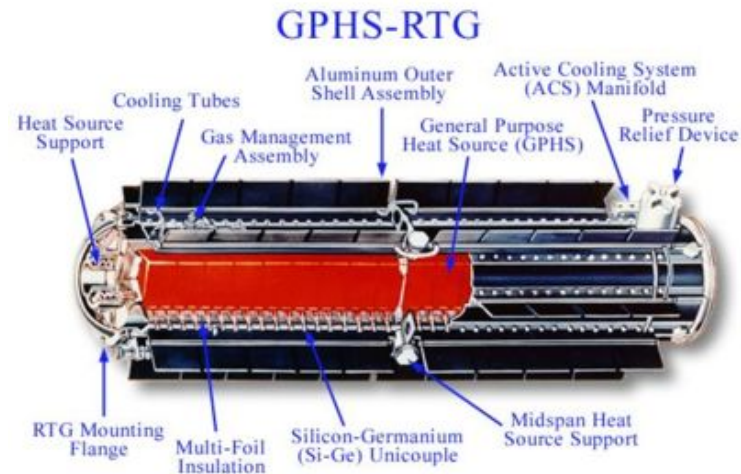
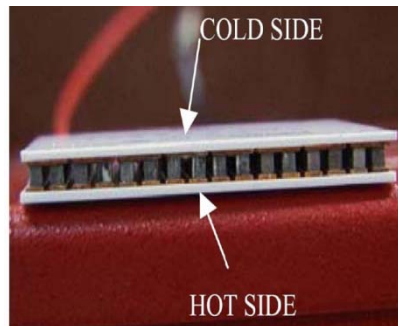
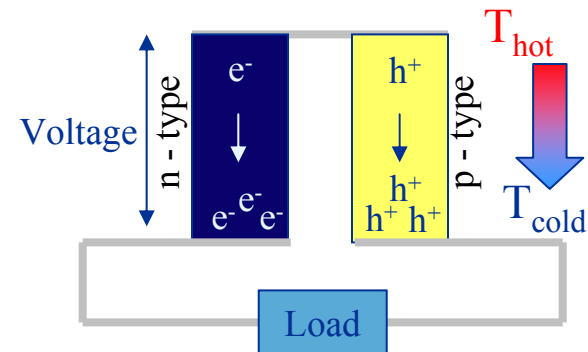
NASA-IVHM

AFOSR (EOARD Grant # 073031)

NASA-Hypersonics (NNX08AB34A)

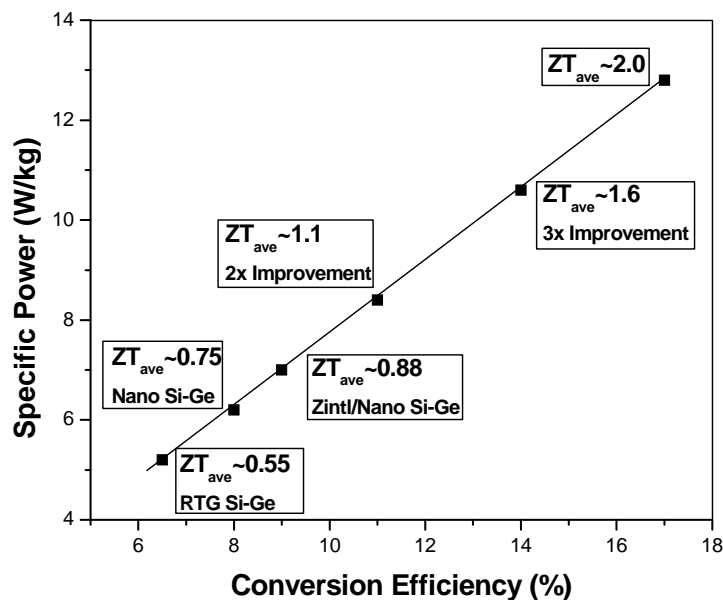


Heat to Electric Power Generation



Objective: High Conversion Efficiency
 • Reduces Mass, Volume & Cost

Space Power Generation



Waste Heat to Power

- Waste Heat is a under utilized energy resource
- U.S.-energy consumption ~ 29 tera-kWh (10^{12})
Barrels of Oil – 170 giga-barrels (10^9)
- World-energy consumption ~ 120 tera- kWh (10^{12})
- 20-65 percent is lost in the form of heat
- Maximizes efficiency
- Reduces CO₂ emission

- High temperature
- Low mass
- Oxidizing environment
- Low cost

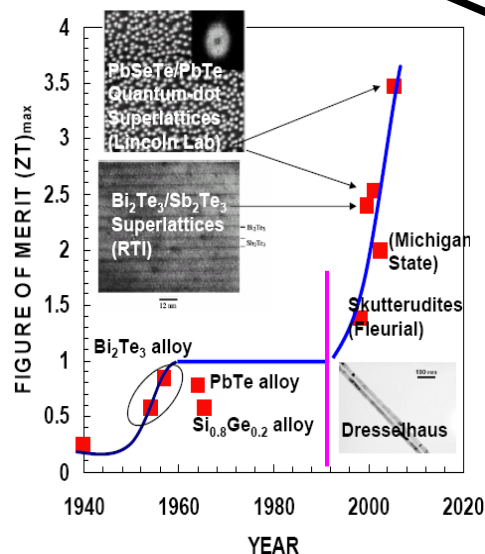
Figure of Merit

$$ZT = \frac{S^2 \sigma}{K} T$$

S - Seebeck coefficient
 σ - electrical conductivity
 K - thermal conductivity

Efficiency

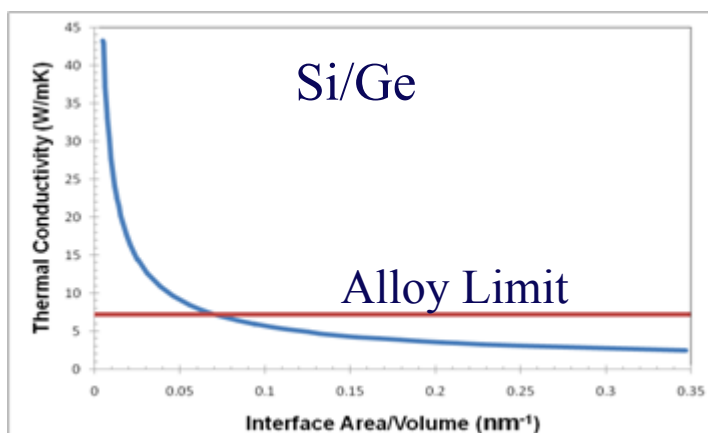
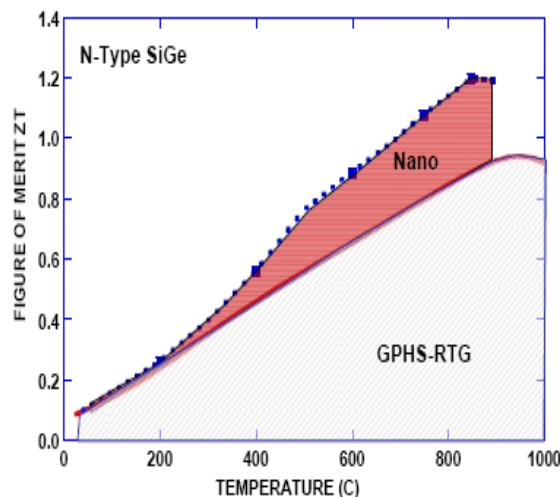
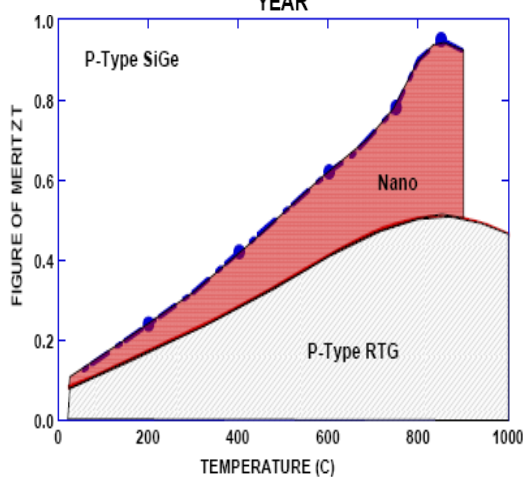
$$\eta_{\max} = \frac{\Delta T}{T_{\text{hot}}} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_{\text{cold}}/T_{\text{hot}}}$$



Phonon Scattering:

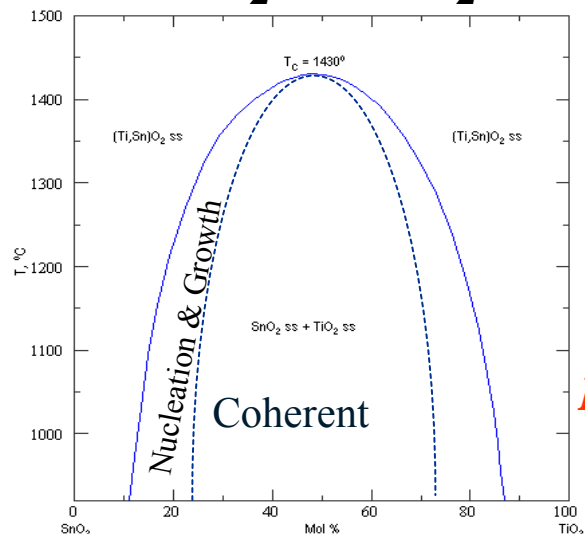
- Atom disorder
- Alloying
- Anharmonic vibrations
- Superlattices
- Crystal Structures
- Nano-technology

Fleural/Chen – JPL/MIT



Spinodal Decomposition

TiO₂ – SnO₂



Desired Features

- ~50 nm grains
- High Temperature Stability
- Wide Composition Range
- Large Δ Mass

Transparent Conducting Oxides

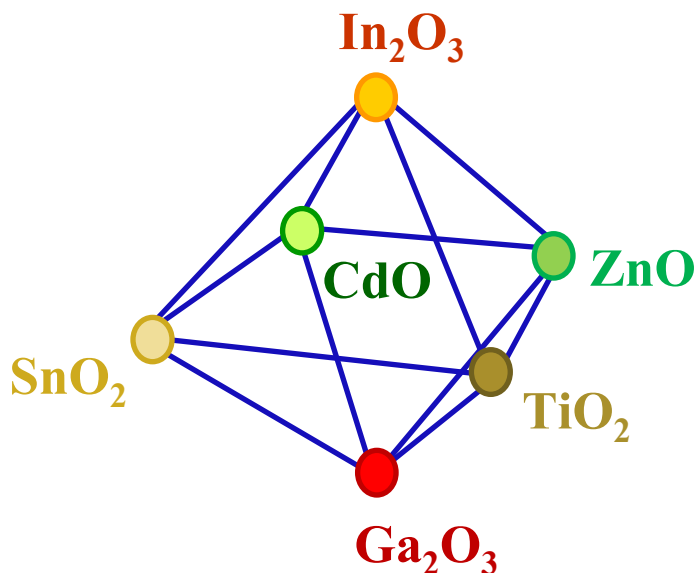
Insulator/Semiconductor/Conductor

- Large Bandgap 2.4-3.8 eV
- N-type – Degenerate Semiconductor



Fig. 10. TEM image of (Ti_{0.5}/Sn_{0.5})O₂ ceramics annealed for 48 h.

Shultz & Stubican, JACS, 53, 1970

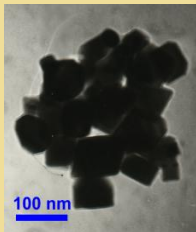


Electrical Conductivity

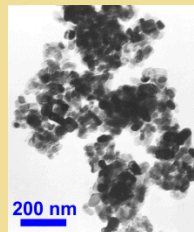
TCO	σ (S/m) @ RT
ITO	8×10^5
In ₂ O ₃	1×10^6
SnO ₂	2.5×10^5
ZnO	8.3×10^5
ZnO:Al	7.7×10^4
CdSnO ₂	7.7×10^5
CdO:In	1.7×10^6

ZnO:Al
ZT~0.6 @ 1000 °C

SnO_2
Purity: 99.9%
APS: 50 nm
SSA: $14.2 \text{ m}^2/\text{g}$



TiO_2 Rutile
Purity: 99.99 %
APS: 20 nm,
SSA: $> 30 \text{ m}^2/\text{g}$



Dopants
 CoO , MnO_2
 Ta_2O_5 , In_2O_3

$\text{TiO}_2/\text{SnO}_2$
50/50 mol %
75/25 mol %
25/75 mol %

Powder
Mixing

Compaction
Die Press

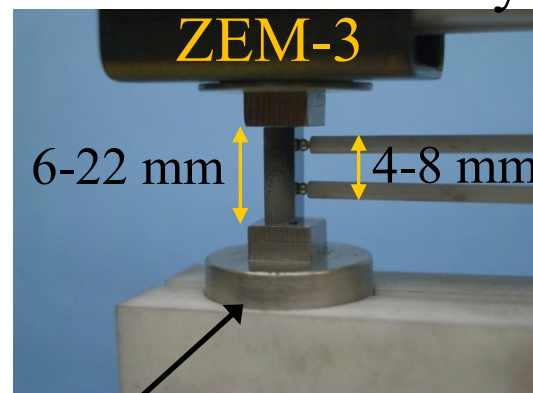
Reactive Sintering
1250-1550 °C

Anneal
72 Hrs

Thermal Conductivity

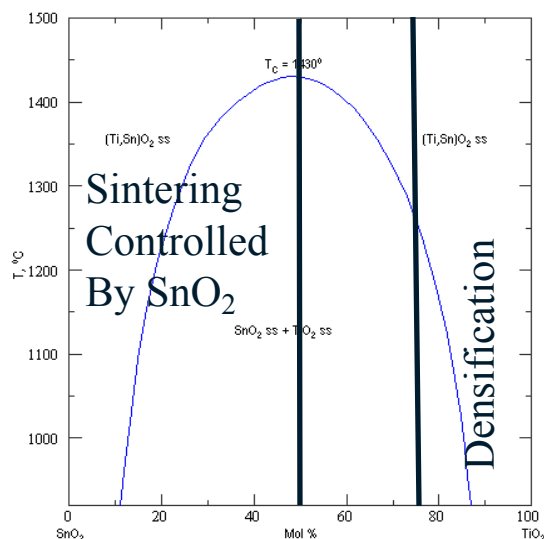
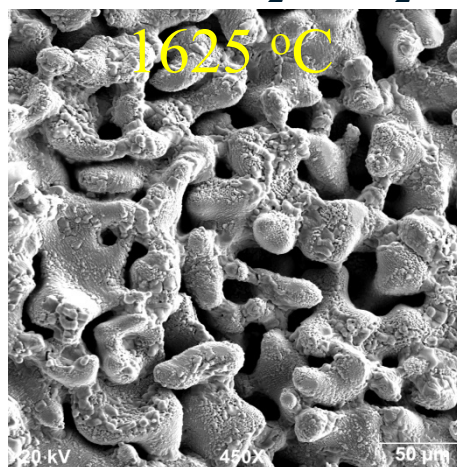
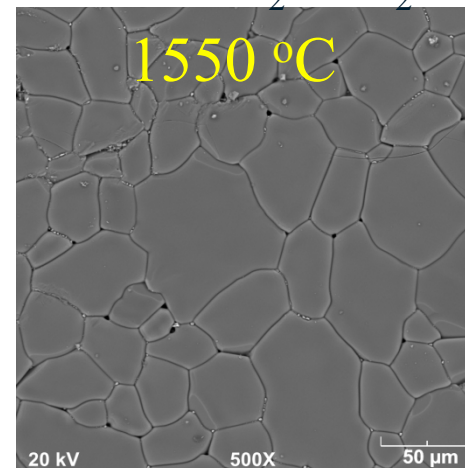
- Laser Flash Method- Thermal Diffusivity
- Standard
- Specific Heat- C_p - Laser Flash
- Thermal Conductivity ($K = \alpha \rho C_p$)

Seebeck/Resistivity



ΔT 0-50 °C/Furnace RT-1000 °C

Sintering

50/50 $\text{TiO}_2/\text{SnO}_2$ 75/25 $\text{TiO}_2/\text{SnO}_2$ 

SnO_2 Sintering-Inhibited

- Surface Diffusion $< 1100^\circ\text{C}$
- Evaporation $> 1100^\circ\text{C}$

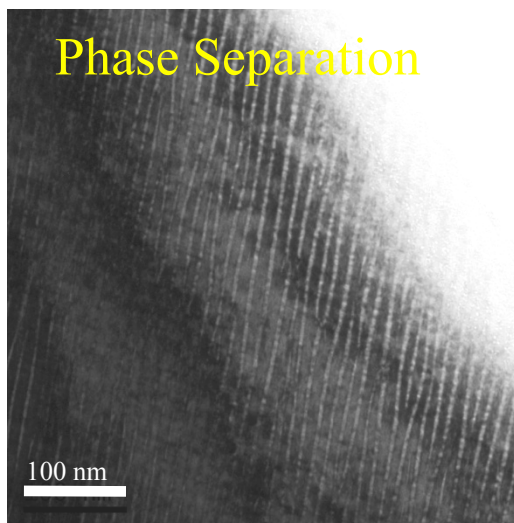


Sintering Aids- SnO_2

- MnO , CoO , CuO , ZnO

50/50 $\text{TiO}_2/\text{SnO}_2$

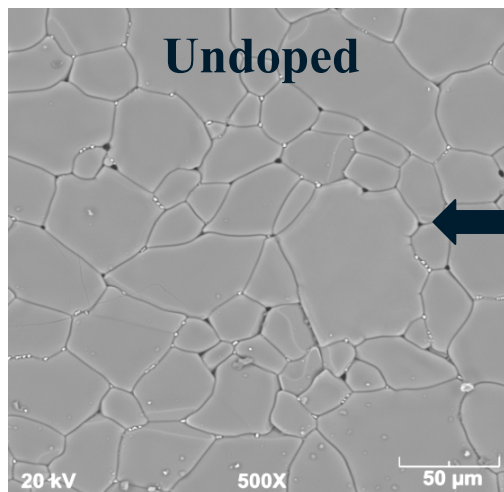
Phase Separation



Ta_2O_5 & In_2O_3
Ineffective Sintering Aids

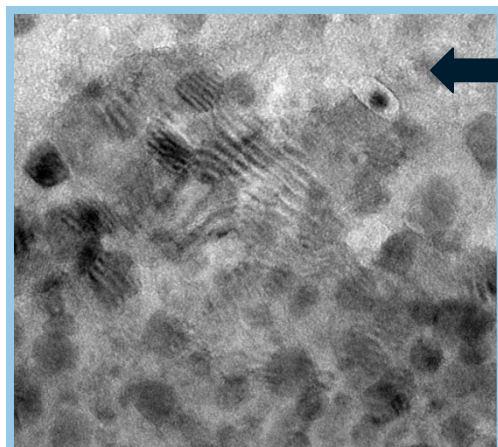
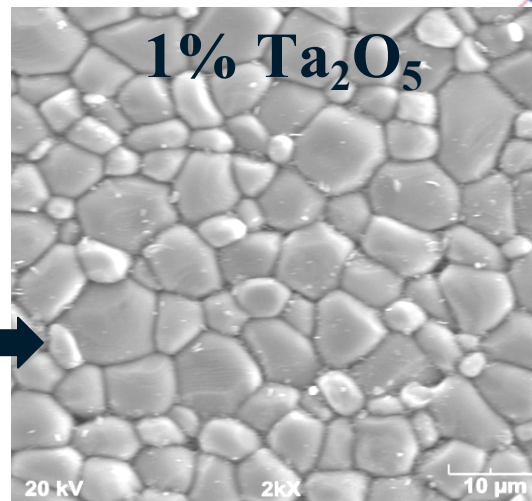


75/25 $\text{TiO}_2/\text{SnO}_2$



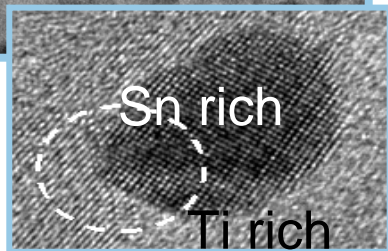
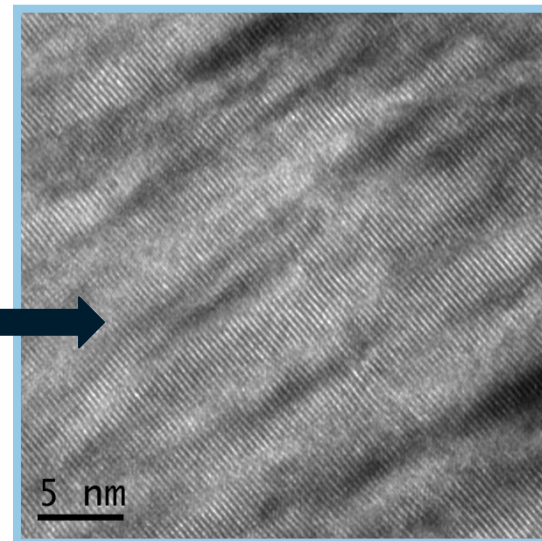
Large Grain

Small Grain

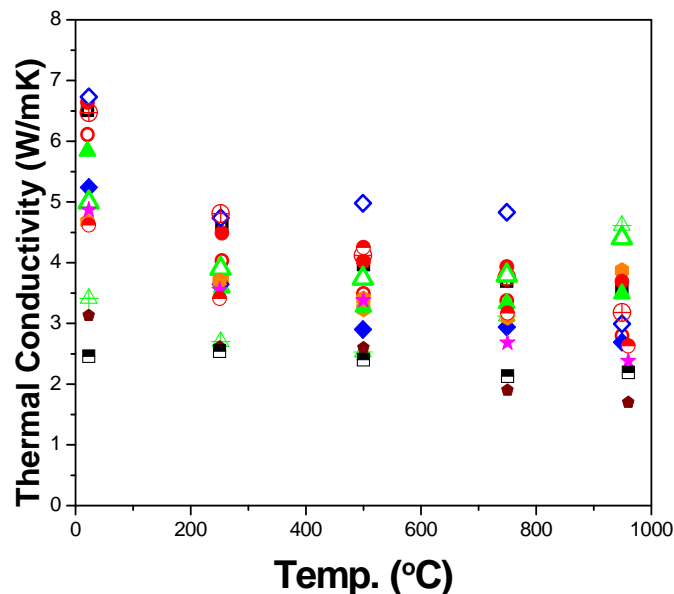
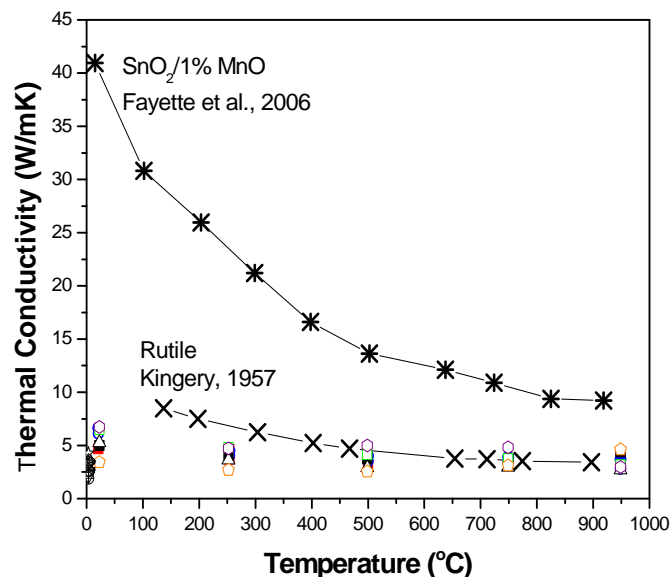


Nano-ppts

Diffuse
Composition
Fluctuation



Thermal Conductivity



Compositions

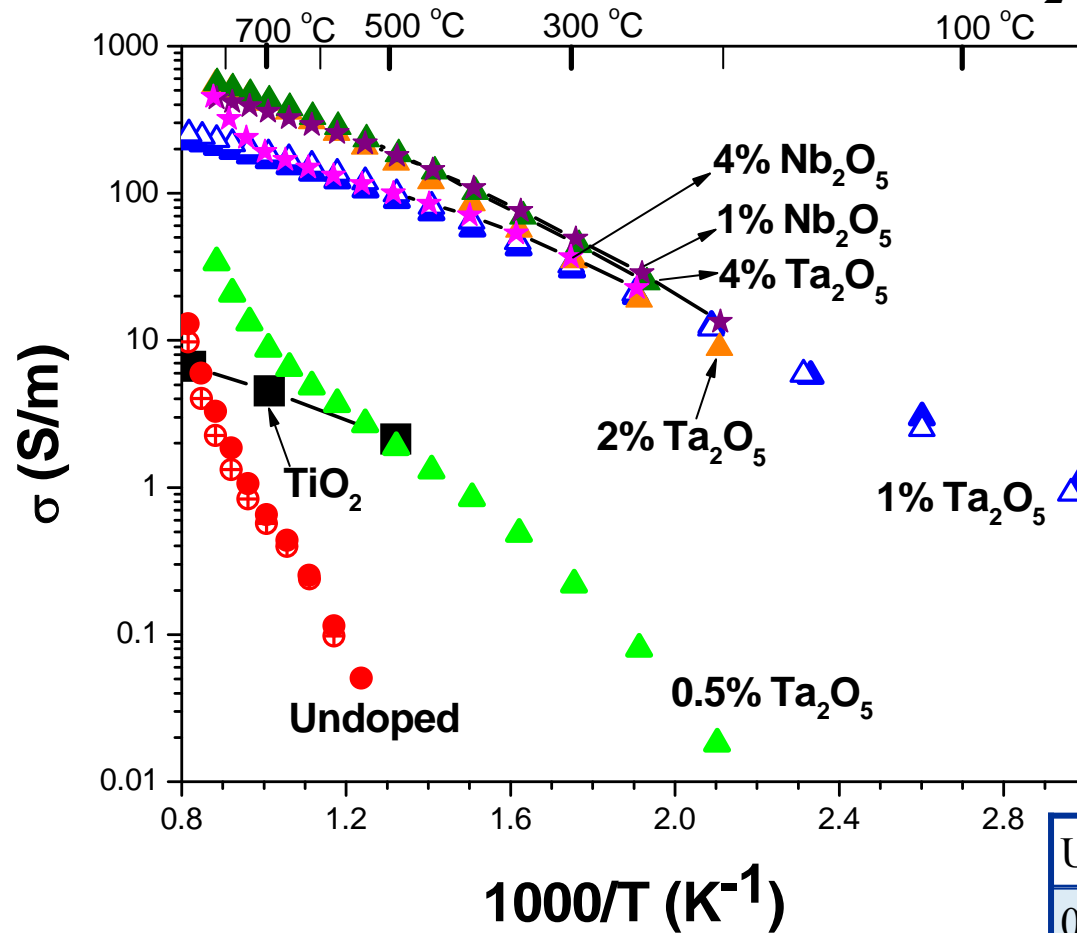
1% MnO-50 TiO₂
 1% CoO-50 TiO₂
 1% MnO-75 TiO₂
 1% CoO-75 TiO₂
 1% MnO-25 TiO₂
 1% CoO- 25TiO₂
 1%Ta₂O₅/0.5%
 CoO-25 TiO₂

- Compositions exhibit low κ – 1.7 to 6.8 W/mK
- Observe no dependence on composition or post treatments
- Spinodal Decomposition – κ reduction ?
- Best ZT ~ 0.05

Electrical Conductivity



75/25 TiO₂/SnO₂



- Ta₂O₅ & Nb₂O₅ - Increases σ
 $M_2O_5 = 2M_{Ti,Sn}^{\bullet} + 2e' + \frac{1}{2}O_2 + 4O_O^X$
- No further σ increase above 2% dopant.
- In₂O₃, MnO & CoO – No σ increase

$$ZT = \frac{S^2 \sigma}{\kappa} T$$

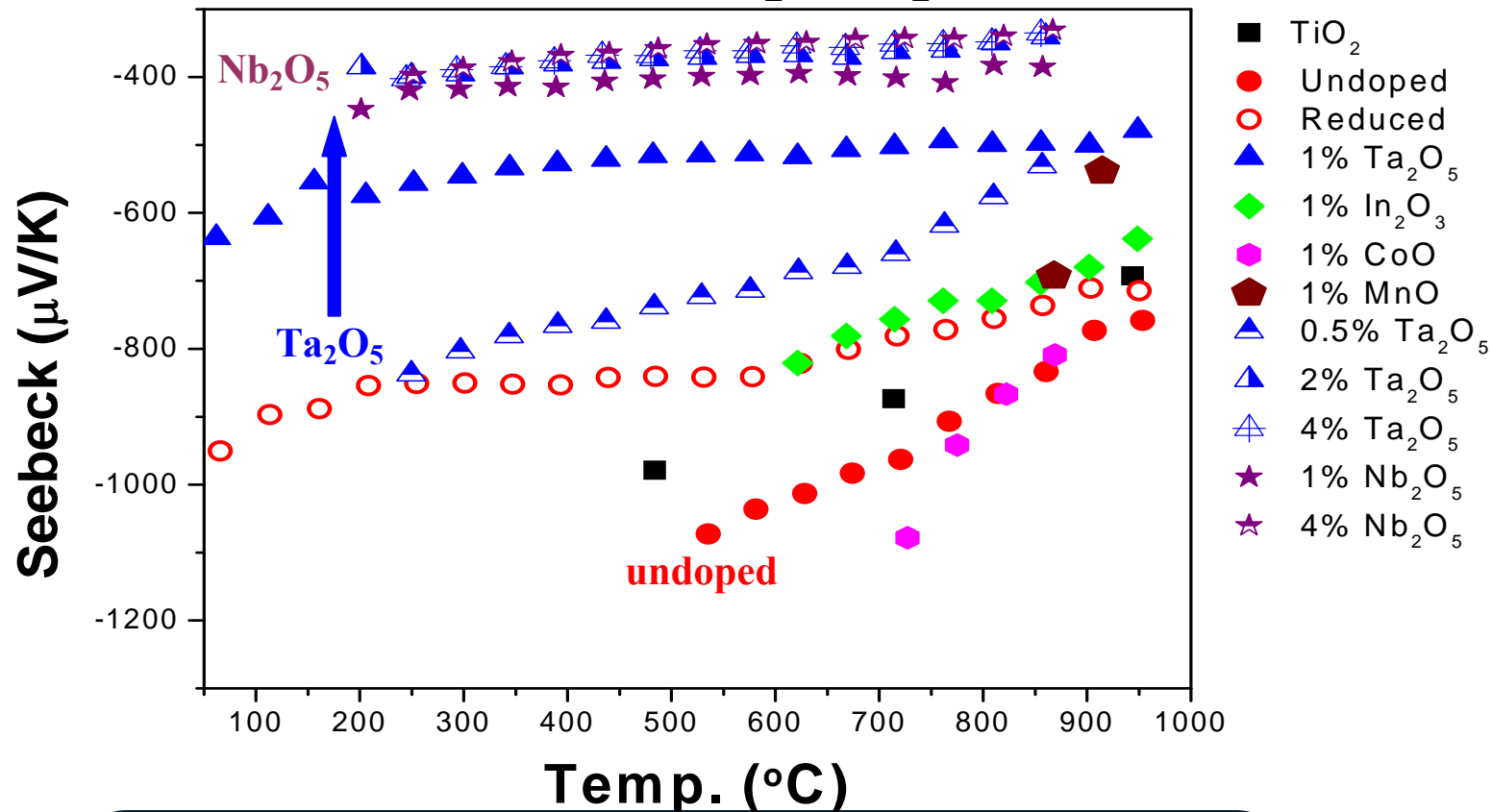
σ to low

Activation Energy

Undoped	0.97 ev	1% Nb ₂ O ₅	0.25 ev
0.5% Ta ₂ O ₅	0.49 ev	4% Nb ₂ O ₅	0.20 ev
1% Ta ₂ O ₅	0.22 ev	1% In ₂ O ₃	0.99 ev
2% Ta ₂ O ₅	0.30 ev	1% CoO	1.6 ev
4% Ta ₂ O ₅	0.26 ev	1% MnO	7.9 ev

Seebeck Coefficient

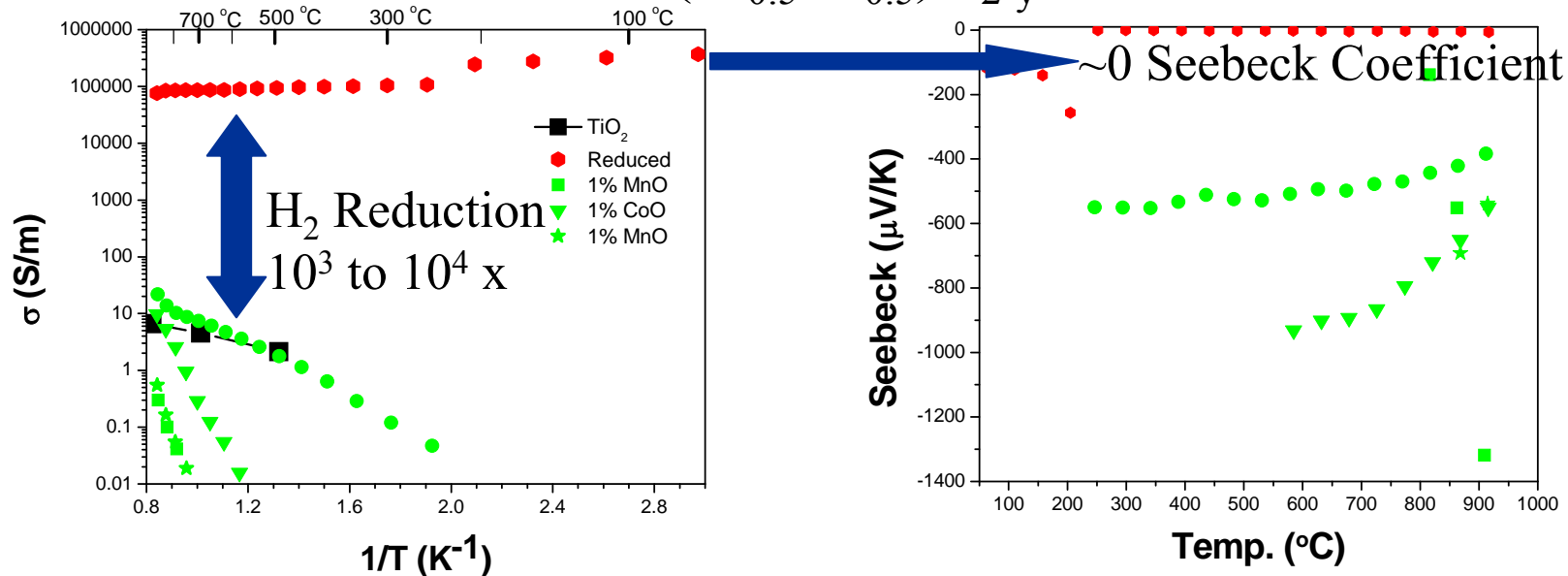
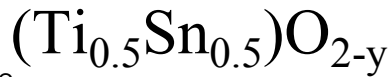
75/25 $\text{TiO}_2/\text{SnO}_2$



- N-type
- Large Seebeck coefficients at low σ
- Increase Ta_2O_5 conc. reduces Seebeck coefficient
- Nb_2O_5 doping most effective in Seebeck reduction



- Improve electrical conductivity by forming oxygen deficient material $(\text{Ti}_x\text{Sn}_{1-x})\text{O}_{2-y}$

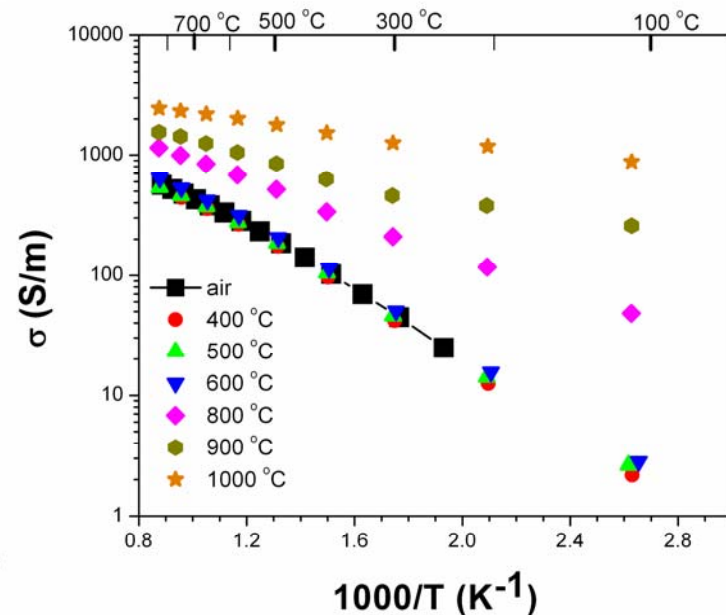
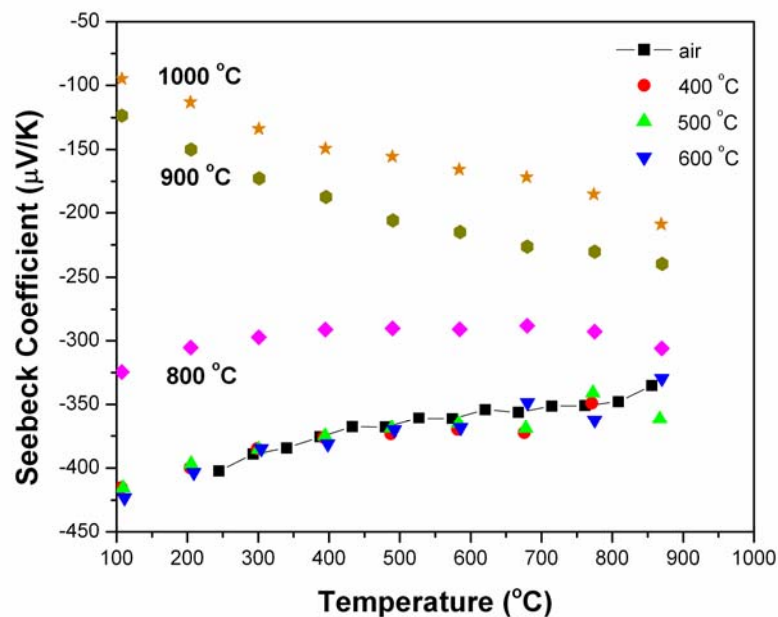


- Control the oxygen stoichiometry to increase σ and maintain a good Seebeck coefficient?

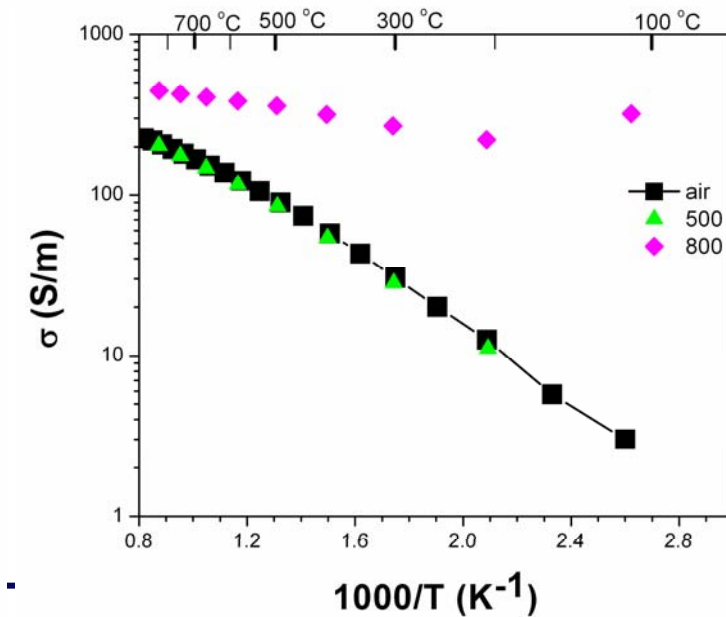
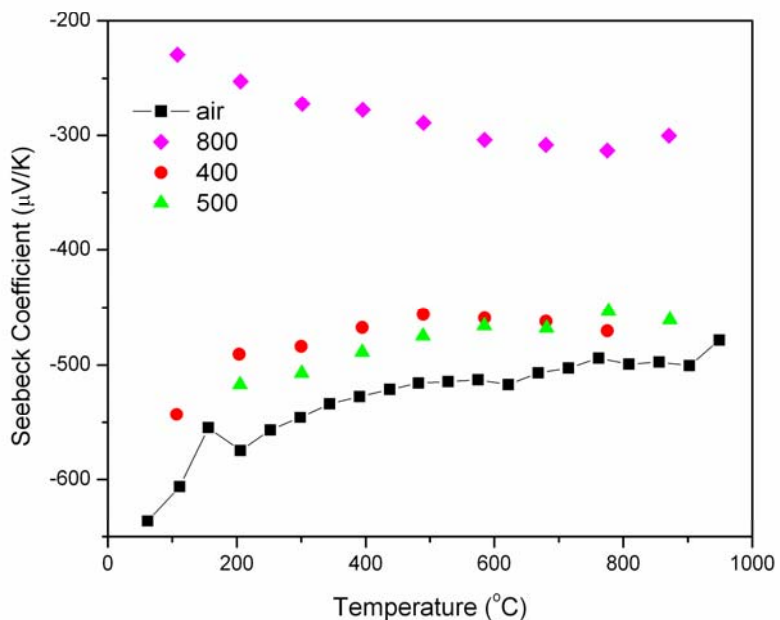
Effects of reducing conditions



4% Ta



1% Ta



Mechanical Robustness

Undoped – 800 °C



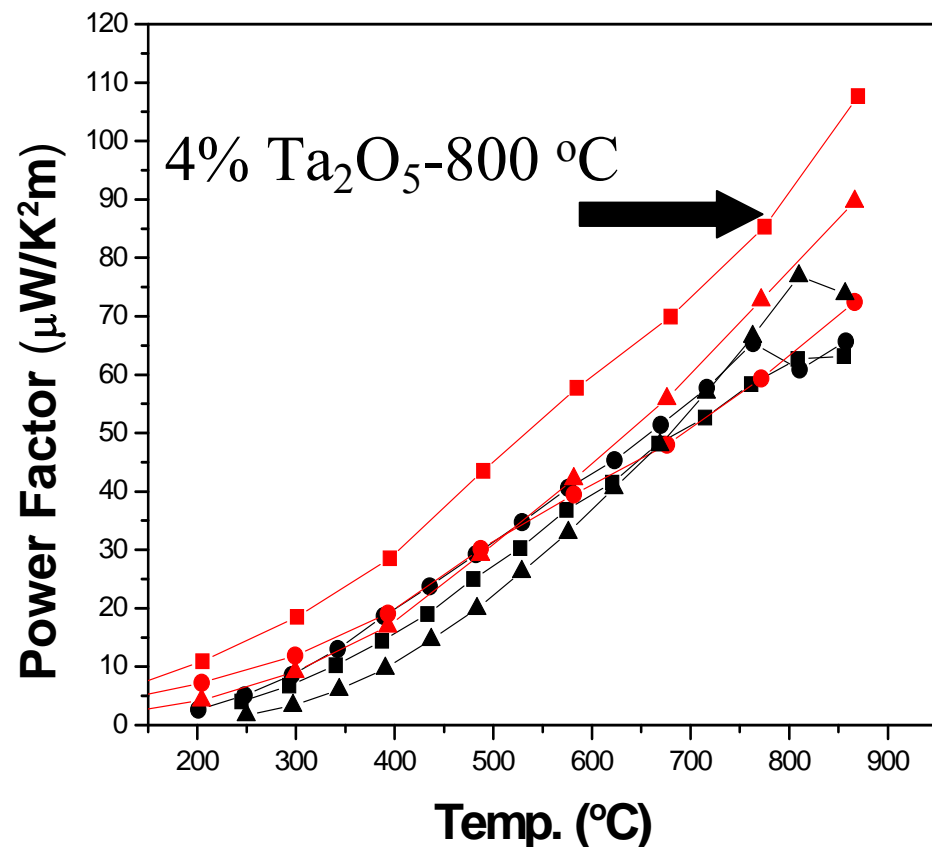
1% Ta doped – 900 °C



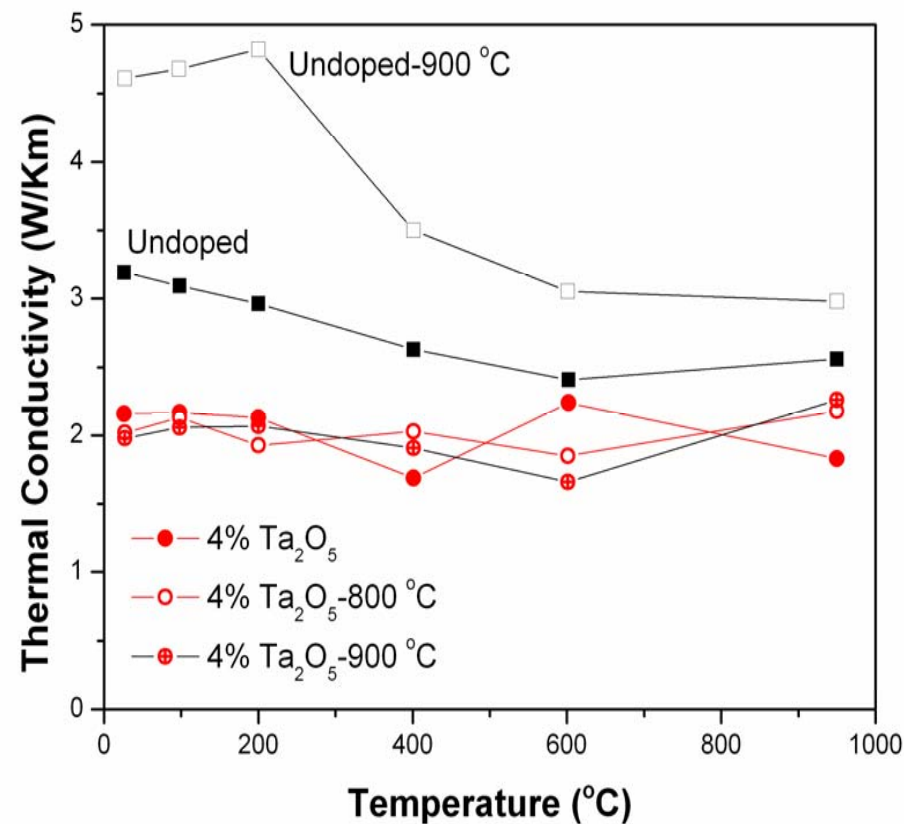
4% Ta doped – 900 °C



Power Factor and Thermal conductivity



$$PF = S^2 \sigma$$





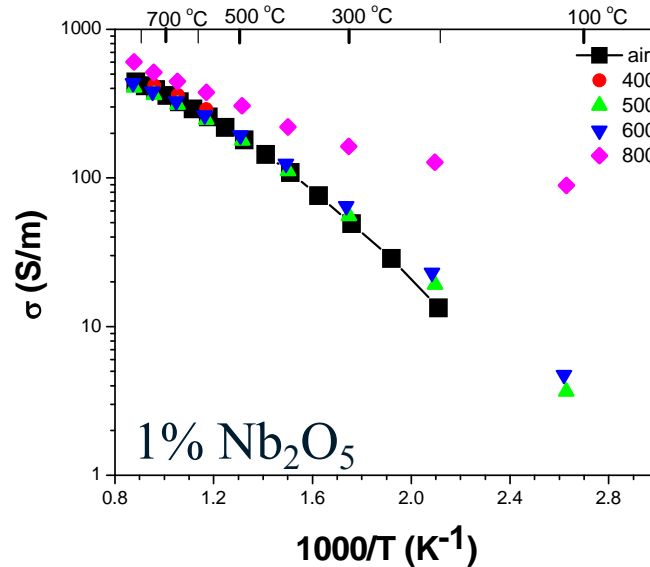
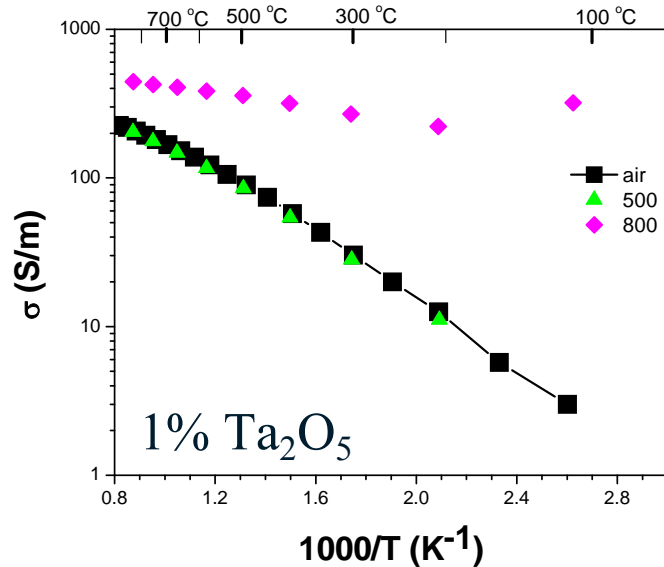
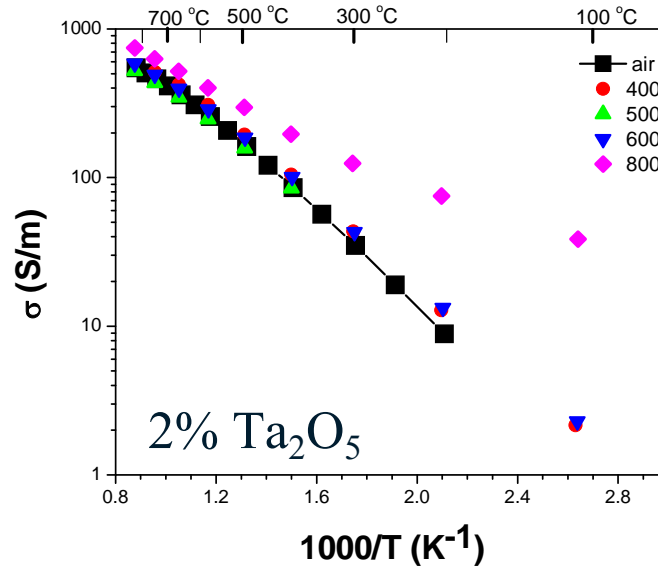
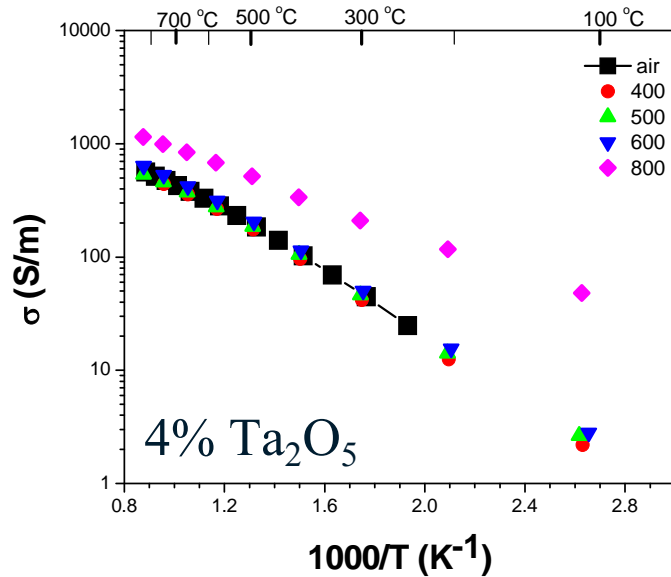
In Summary

- $\text{TiO}_2/\text{SnO}_2$ compositions exhibit low thermal conductivity. Nanostructured phases are observed.
- Improved electrical conductivity is observed for Ta_2O_5 doped $(\text{Ti}_{0.75}\text{Sn}_{0.25})\text{O}_{2-x}$ reduced at 800 °C.
- Reduction of doped samples retained a low thermal conductivity ($\approx 2\text{ W/mK}$).
- 800 °C reduction increases the power factor by 1.69 – 2.76 for 4% Ta_2O_5 doping. However, ZT is < 0.1 .

Dense specimens with Sn-rich compositions need to be evaluated

Acknowledgements

Thomas Sabo
Raymond Babuder



• ≥ 800 °C treatment is Required to enhance σ .

• 4% Ta_2O_5 produces the highest σ .

• Significant effect on low temperature σ .